Effect of organo-fluorine compounds on the thermal stability and electrochemical properties of electrolyte solutions for lithium ion batteries

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HIGHLIGHTS

► Reactivity of metallic Li with fluorine compounds is much lower than that of EC/DMC.
► Reactivity of LiC_6 with fluorine compound-mixed electrolyte solutions containing $LiPF_6$ is low.
► Oxidation currents in fluorine-compound-mixed solutions are smaller than those in original ones.
► First coulomic efficiencies are high in fluoro-ether-mixed electrolyte solutions.

ARTICLE INFO

ABSTRACT

Thermal stability and electrochemical behavior of fluorine compound-mixed electrolyte solutions have been investigated using 1 $molL^{-1}$ $LiClO_4$-EC/DEC/PC, 1 $molL^{-1}$ $LiPF_6$-EC/DMC and 1 $molL^{-1}$ $LiPF_6$-EC/EMC/PC. DSC study indicates that no exothermic reaction occurs between metallic Li and fluoro-ethers while EC/DMC mixture and fluoro-carbonate start to react with Li at 180 and 226 °C, respectively. In $LiClO_4$-containing electrolyte solution, lithiated graphite easily reacts with surface film and electrolyte solutions with and without fluoro-ethers, giving exothermic peaks at 153–162 °C. However, exothermic peaks at 111–137 °C caused by the reaction of lithiated graphite with surface film and electrolyte solutions are weak in $LiPF_6$-containing solutions probably because LiF contained in the surface film prevents the reaction with deintercalated Li. Fluoro-carbonate-mixed solution gives the lower reactivity with deintercalated Li than fluoro-ether-mixed ones. Electrochemical oxidation currents are decreased by mixing of fluoro-ethers in both $LiClO_4$- and $LiPF_6$-containing electrolyte solutions. Charge/discharge experiments indicate that first coulombic efficiencies of natural graphite are mostly high in fluoro-ether-mixed electrolyte solutions, and fluoro-ethers facilitate the formation of surface film on graphite in PC-containing solutions.

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1. Introduction

High safety is one of the most important issues for lithium ion batteries since they use flammable organic solvents. It is particularly requested for their application to hybrid cars and electric vehicles. To improve the thermal stability of lithium ion batteries, many kinds of phosphorus compounds such as phosphates were investigated [1–27]. It was shown that they provide flame retarding properties to electrolyte solutions. Other compounds such as phosphazenes, borate, triazines and so on were also examined as flame retardants [28–34]. Organo-fluorine compounds are another type of candidates as non-flammable solvents because they have normally high oxidation stability. Thermal stability and electrochemical properties were investigated using fluorine-containing ethers, esters and carbonates [35–44]. It was found more than 10 years ago that fluoro-ethers and fluoro-esters improve charge/discharge characteristics of graphite electrode at low temperatures less than 0 °C [45,46]. This work was extended to our recent study on the oxidation stability and electrochemical properties of fluorine compound-mixed electrolyte solutions [39–41]. Fluorine substitution of organic compounds usually improves their oxidation stability and simultaneously elevates reduction potentials. As expected, both HOMO and LUMO levels of fluorine-containing carbonates, esters and ethers are lower than those of the same type compounds without fluorine [39,40]. It was recently reported

that mixing of organo-fluorine compounds with electrolyte solutions improves oxidation stability [35–44]. However, it is also important to investigate charge/discharge behavior of graphite electrode in low potential region because fluorine-containing carbonates, esters and ethers are electrochemically reduced at higher potentials than usually employed organic solvents such as EC (ethylene carbonate), PC (propylene carbonate), DMC (dimethyl carbonate), EMC (ethyl methyl carbonate) and DEC (diethyl carbonate). Synthetic and natural graphites are normally used as anode materials [39–41]. For these graphites with high crystallinity, EC-based solvents should be employed for the quick formation of surface film (Solid Electrolyte Interphase: SEI). Since EC has a high melting point (36 °C), it is desirable to use PC with a low melting point (−55 °C). However, it is difficult to use PC for graphite with high crystallinity because electrochemical reduction continues on graphite, which gives a large irreversible capacity. Therefore, fluorine compounds are very useful if they facilitate SEI formation on graphite electrode. The advantage of fluorine-containing carbonates and ethers for the SEI formation was shown in our previous papers [39–41].

In the present study, thermal stability and electrochemical oxidation stability of fluoro-ether-mixed electrolyte solutions have been investigated using 1 molL^{-1} LiClO$_4$-EC/DEC/PC, 1 molL^{-1} LiPF$_6$-EC/DMC and 1 molL^{-1} LiPF$_6$-EC/EMC/PC. Fluoro-carbonate-mixed solution was also used for comparison. To confirm the influence of electrochemical reduction of fluorine compounds, charge/discharge behavior of natural graphite powder has been evaluated in the fluorine compound-mixed electrolyte solutions.
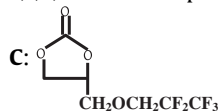
2. Experimental

2.1. Organo-fluorine compounds

The following fluoro-ethers and fluoro-carbonate (purity: 99.9%, H$_2$O: <10 ppm), synthesized in Daikin Industries, Ltd., were used in the present study.

A: **HCF$_2$CF$_2$CH$_2$OCF$_2$CF$_2$H** 3-(1,1,2,2-tetrafluoroethoxy)-1,1,2,2-tetrafluoropropane.
B: **HCF$_2$CF$_2$CH$_2$OCF$_2$CFClH** 3-(2-chloro-1,1,2-trifluoroethoxy)-1,1,2,2-tetrafluoropropane

C:

4-(2,2,3,3,3-pentafluoropropoxymethyl)-[1,3]dioxolan-2-one

Viscosities, dielectric constants, surface tensions and boiling points of **A** and **B** are 1.60 and 1.46 mPa s; 6.4 and 6.3; 20.2 and 21.6 mNm^{-1}, and 92 and 107 °C, respectively.

2.2. Thermal stability by DSC measurements

Thermal stability of fluoro-ether or carbonate-mixed electrolyte solutions was examined by differential scanning calorimetry (DSC-60, Shimadzu). DSC measurement was carried out using a mixture of electrolyte solution with or without fluorine compound and lithiated or delithiated graphite (NG15 μm) between room temperature and 300 °C at a temperature increasing rate of 5 °C min^{-1}. Fluorine compound-mixed electrolyte solutions used were 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC (**A** or **B**) (1:1:1:1.5 vol.), 1 molL^{-1} LiPF$_6$-EC/DMC/(**A**, **B** or **C**) (1:1:1 vol.) and 1 molL^{-1} LiPF$_6$-EC/EMC/PC/(**A** or **B**) (1:1:1:1.5 vol.). Thermal stability of only lithiated graphite without electrolyte solution, and reaction of metallic
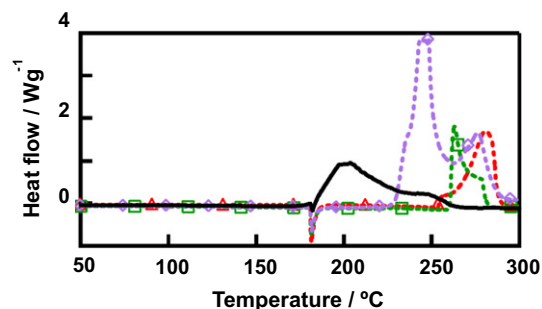

Fig. 1. DSC curves for mixtures of metallic Li and EC/DMC (1:1 vol.) or fluorine compound (**A**, **B** or **C**). ———: EC/DMC, − − −△− − −: fluoro-ether **A**, − − −☐− − −: fluoro-ether **B**, − − −◇− − −: fluoro-carbonate **C**.

Li with EC/DMC mixture (1:1 vol.) or fluorine compound **A**, **B** or **C** were also checked in the same manner. Fully lithiated and delithiated graphite samples were electrochemically prepared after 3 cycles. Li-intercalated graphite samples were Li$_{0.91-0.99}$C$_6$ prepared in LiClO$_4$ solution (0.8–1.2 mg used for DSC) and Li$_{0.88-0.98}$C$_6$ prepared in LiPF$_6$ solution (1.3–1.7 mg used for DSC). Electrolyte solution and metallic Li used for DSC measurements were 3 μL and 9.0–11.0 mg, respectively.

2.3. Electrochemical oxidation stability by oxidation current measurements

Oxidation currents were measured by linear sweep of potential at 0.1 mVs^{-1} between 4 and 10 V vs Li/Li$^+$ for 0.90, 0.78 or 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC (1:1:1 vol.) and 0.90, 0.78 or 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/(**A** or **B**) (1:1:1:0.33, 0.83 or 1.5 vol.,
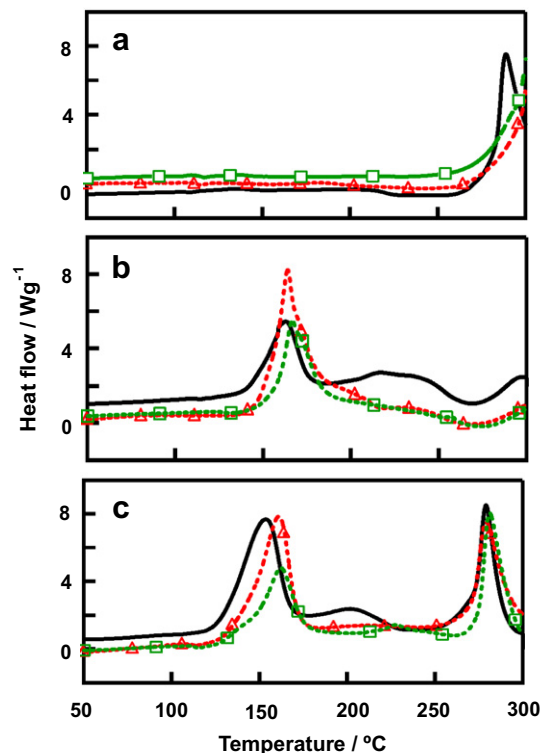

Fig. 2. DSC curves for mixtures of 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC (1:1:1 vol.) or 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/(**A** or **B**) (1:1:1:1.5 vol.) and delithiated graphite with SEI film (a), only lithiated graphite (Li$_{0.91-0.99}$C$_6$) (b), and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC (1:1:1 vol.) or 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/(**A** or **B**) (1:1:1:1.5 vol.) and lithiated graphite (Li$_{0.91-0.99}$C$_6$) (c). ———: EC/DEC/PC, − − −△− − −: EC/DEC/PC/**A**, − − −☐− − −: EC/DEC/PC/**B**.
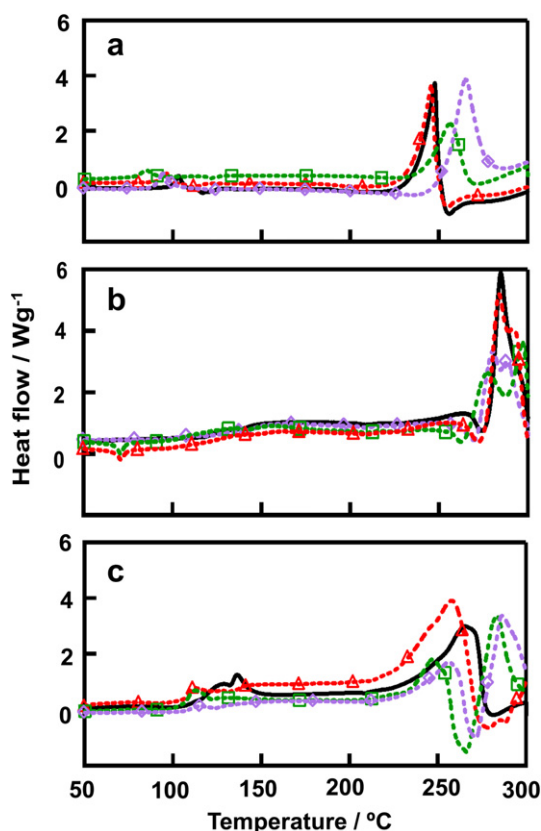
Fig. 3. DSC curves for mixtures of 1 molL^{-1} LiPF$_6$-EC/DMC (1:1 vol.) or 1 molL^{-1} LiPF$_6$-EC/DMC/(**A**, **B** or **C**) (1:1:1 vol.) and delithiated graphite with SEI film (a), only lithiated graphite (Li$_{0.90-0.98}$C$_6$) (b), and 1 molL^{-1} LiPF$_6$-EC/DMC (1:1 vol.) or 1 molL^{-1} LiPF$_6$-EC/DMC/(**A**, **B** or **C**) (1:1:1 vol.) and lithiated graphite (Li$_{0.90-0.98}$C$_6$) (c). ——: EC/DMC, – –△– –: EC/DMC/**A**, – –☐– –: EC/DMC/**B**, – –◇– –: EC/DMC/**C**.

10.0, 21.7 or 33.3 vol.%, respectively) by using Pt wire electrode (diameter: 0.3 mm, geometrical surface area: 0.22 cm^2), and 1 molL^{-1} LiPF$_6$-EC/DMC (1:1 vol.) and 1 molL^{-1} LiPF$_6$-EC/DMC/(**A** or **B**) (1:1:1 vol.) by using glassy carbon electrode (diameter: 2.93 mm,
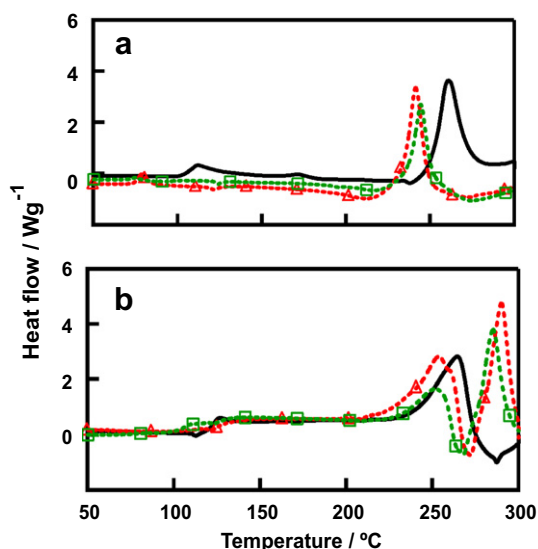
Fig. 4. DSC curves for mixtures of 1 molL^{-1} LiPF$_6$-EC/EMC/PC (1:1:1 vol.) or 1 molL^{-1} LiPF$_6$-EC/EMC/PC/(**A** or **B**) (1:1:1:1.5 vol.) and delithiated graphite with SEI film (a), and 1 molL^{-1} LiPF$_6$-EC/EMC/PC (1:1:1 vol.) or 1 molL^{-1} LiPF$_6$-EC/EMC/PC/(**A** or **B**) (1:1:1:1.5 vol.) and lithiated graphite (Li$_{0.88-0.92}$C$_6$) (b). ——: EC/EMC/PC, – –△– –: EC/EMC/PC/**A**, – –☐– –: EC/EMC/PC/**B**.
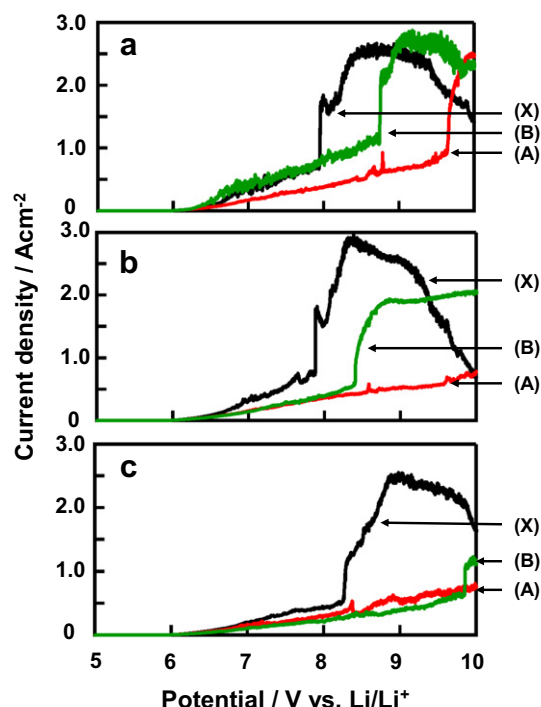

Fig. 5. Linear sweep voltammograms for Pt wire electrode in fluoro-ether-mixed electrolyte solutions. (a) 0.90 molL^{-1} LiClO$_4$-EC/DEC/PC (1:1:1 vol.) and 0.90 molL^{-1} LiClO$_4$-EC/DEC/PC/(**A** or **B**) (1:1:1:0.33 vol.), (b) 0.78 molL^{-1} LiClO$_4$-EC/DEC/PC (1:1:1 vol.) and 0.78 molL^{-1} LiClO$_4$-EC/DEC/PC/(**A** or **B**) (1:1:1:0.83 vol.), (c) 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC (1:1:1 vol.) and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/(**A** or **B**) (1:1:1:1.5 vol.). (X): EC/DEC/PC, (A): EC/DEC/PC/**A**, (B): EC/DEC/PC/**B**.

geometrical surface area: 1.73 cm^2) (Hokuto Denko, HZ-5000). The 1 molL^{-1} LiPF$_6$-EC/DMC/(**A** or **B**) was prepared by dissolving LiPF$_6$ into fluoro-ether-mixed electrolyte solutions. Counter and reference electrodes were Li foil.

2.4. Charge/discharge behavior for NG15 μm electrode in fluorine compound-mixed electrolyte solutions

Natural graphite (purity: >99.95%) with average particle size of 15 μm (abbreviated to NG15 μm) was used as an electrode material. The d_{002} value obtained by X-ray diffractometry (XRD-6100, Shimadzu) was 0.3355 nm. Surface area and meso-pore volume obtained by BET surface area measurement (Tristar 3000, Shimadzu) were 6.9 m^{2}g^{-1}, and 0.026 cm^{3}g^{-1}. Peak intensity ratios of D-band to G-band ($R = I_D/I_G$) obtained by Raman spectroscopy (NRS-1000, Jasco) with Nd:YVO$_4$ laser (532 nm) was 0.25.

Three-electrode cell with natural graphite as a working electrode and Li foil as counter and reference electrodes was used for galvanostatic charge/discharge experiments. Natural graphite electrode was prepared as follows. Natural graphite powder was dispersed in N-methyl-2-pyrrolidone (NMP) containing 12 wt% poly(vinylidene fluoride) (PVdF) and the slurry was pasted on a copper current collector. The electrode was dried at 120 °C under vacuum for half a day. After drying, the electrode contained 80 wt% graphite and 20 wt% PVdF. Electrolyte solutions were prepared by mixing fluorine compound with 1 molL^{-1} LiClO$_4$−EC/DEC/PC (1:1:1 vol.), 1 molL^{-1} LiPF$_6$-EC/DMC (1:1 vol.) and 1 molL^{-1} LiPF$_6$-EC/EMC/PC (1:1:1 vol.). The fluorine compounds are miscible with 1 molL^{-1} LiClO$_4$-EC/DEC/PC in whole range of composition at room temperature. The 0.90, 0.78 or 0.67 molL^{-1} LiClO$_4$−EC/DEC/PC/(**A** or **B**) (1:1:1:0.33, 0.83 or 1.5 vol., 10.0, 21.7 or 33.3 vol.%, respectively) was used for galvanostatic charge/discharge experiments.
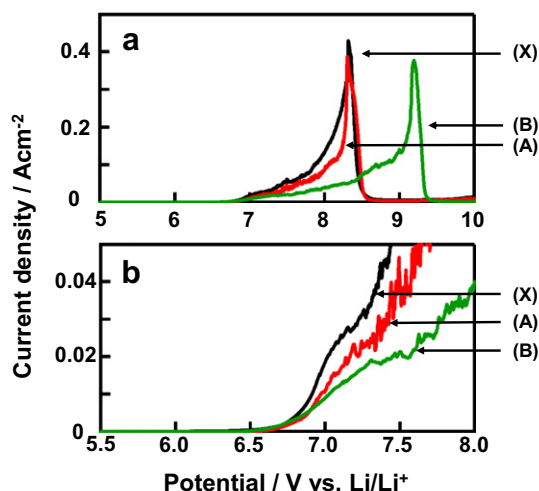
Fig. 6. Linear sweep voltammograms for glassy carbon electrode in fluoro-ether-mixed electrolyte solutions. (a) 1 molL^{-1} LiPF$_6$-EC/DMC (1:1 vol.) and 1 molL^{-1} LiPF$_6$-EC/DMC/(**A** or **B**) (1:1:1 vol.), and (b) magnified figure between 5.5 and 8.0 V. (x): EC/DMC, (A): EC/DMC/**A**, (B): EC/DMC/**B**.

Preparation of 1 molL^{-1} LiClO$_4$–EC/DEC/PC/(**A** or **B**) (1:1:1:1.5 vol., 33.3 vol.%) can be made at room temperature by dissolving LiClO$_4$ into 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/(**A** or **B**) (1:1:1:1.5 vol., 33.3 vol.%), respectively. In case of LiPF$_6$-dissolved electrolyte solutions,

1 molL^{-1} LiPF$_6$-EC/DMC/(**A**, **B** or **C**) and 1 molL^{-1} LiPF$_6$-EC/EMC/PC/ (**A** or **B**) were used by dissolving LiPF$_6$ into fluorine compound-mixed electrolyte solutions. Galvanostatic charge/discharge cyclings were performed using NG15 μm at current densities of 60, 150 and 300 mA g^{-1} between 0 and 3 V relative to Li/Li$^+$ reference electrode at 25 °C (Hokuto Denko, HJ1001 SM8A).

3. Results and discussion

3.1. Thermal stability of fluorine compound-mixed electrolyte solutions

Reaction of metallic Li with a solvent mixture EC/DMC (1:1 vol.) or fluorine compound (**A**, **B** or **C**) was examined as shown in Fig. 1. No reaction occurred below 180 °C because the melting point of metallic Li is 180 °C (endothermic peak at 180 °C) and Li surface is protected by oxide film. After 180 °C, exothermic reaction of Li with EC/DMC was observed in the range of 180–260 °C. It is known that EC and DMC react with Li to give lithium alkyl carbonates and lithium alkoxide such as (CH$_2$OCO$_2$Li)$_2$, CH$_3$OCO$_2$Li and CH$_3$OLi [47–49]. Reaction of Li with partially fluorinated carbonate **C** started at much higher temperature of 226 °C. This would be due to the lower electron density of oxygen atom in >C=O group of fluoro-carbonate **C** than that of EC by the effect of fluorine having an electron-withdrawing ability. EC more easily accepts electron from Li than **C**, yielding Li salts. Fluoro-ethers **A** and **B** are stable against
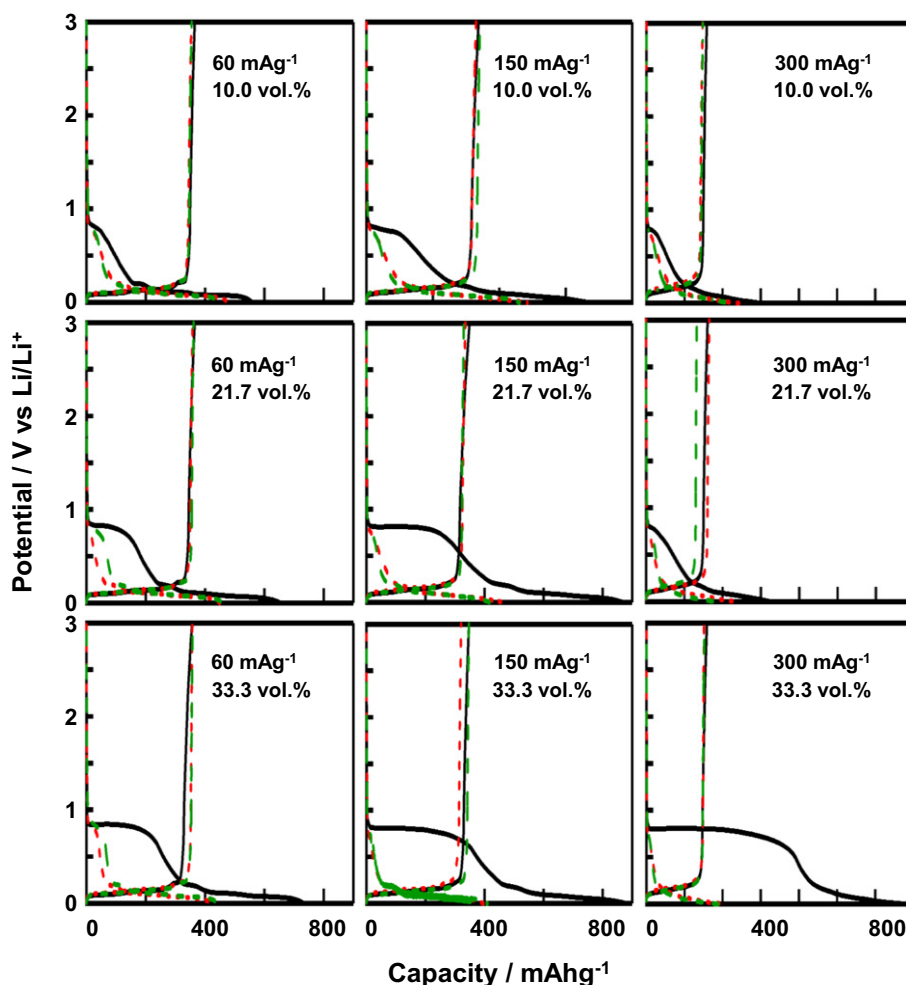

Fig. 7. Charge/discharge potential curves at 1st cycle, obtained in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC (1:1:1 vol.), and 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/(**A** or **B**) (1:1:1:0.33, 0.83 or 1.5 vol.) at current densities of 60, 150 and 300 mAg^{-1}. ——————: EC/DEC/PC, - - - - - - -:EC/DEC/PC/**A**, – – – – – : EC/DEC/PC/**B**.
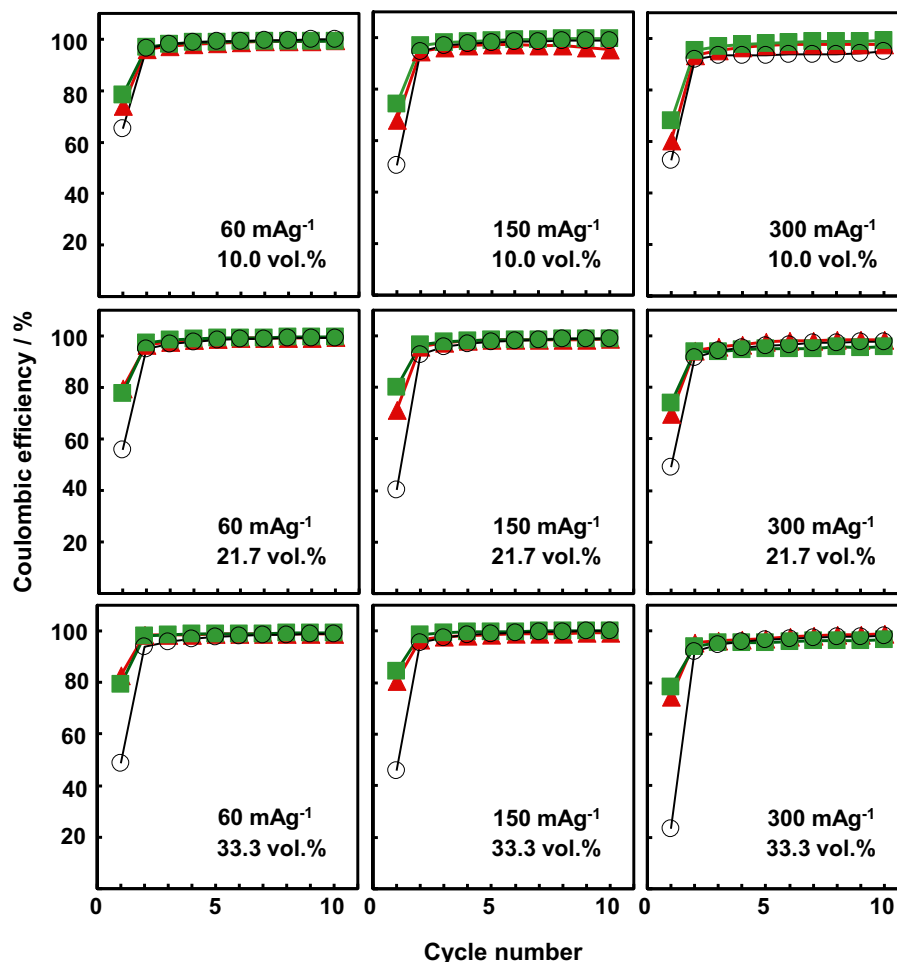
Fig. 8. Coulombic efficiencies as a function of cycle number, obtained in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC (1:1:1 vol.), and 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/ (**A** or **B**) (1:1:1:0.33, 0.83 or 1.5 vol.) at current densities of 60, 150 and 300 mAg^{-1}. ——⊖——: EC/DEC/PC, ——▲——: EC/DEC/PC/**A**, ——■——: EC/DEC/PC/**B**.

Li. Exothermic peaks started at the higher temperatures than those for EC/DMC and **C**, i.e. 254 °C and 261 °C for **A** and **B**, respectively, which are close to thermal decomposition temperatures of organic compounds.

Fig. 2 shows DSC data obtained by using LiClO$_4$-containing electrolyte solution. No exothermic peak was observed below 260 °C for the mixtures of electrolyte solution and delithiated graphite (Fig. 2(a)). Exothermic peaks indicating thermal decomposition of SEI on graphite and electrolyte solution were found at 286 °C and above 300 °C. Fig. 2(b) was obtained for only lithiated graphites (Li$_{0.91-0.99}$C$_6$) without electrolyte solutions. Exothermic peaks were located at 164–169 °C for all samples prepared in the electrolyte solutions with and without fluoro-ethers **A** and **B**, indicating the reactions of deintercalated fresh Li with SEI. Mixtures of electrolyte solution and lithiated graphite (Li$_{0.91-0.99}$C$_6$) provided two exothermic peaks at 153–162 °C and 280 °C (Fig. 2(c)). The peaks at 153–162 °C and 280 °C would be due to reactions of deintercalated Li with SEI and electrolyte solution, and thermal decomposition of SEI and electrolyte solution, respectively. Effect of fluoro-ethers **A** and **B** on the reaction with deintercalated Li is small because the exothermic peaks shifted only from 153 to 162 °C by mixing of fluoro-ethers. This may be because fluoro-ethers mainly interact with hydrocarbon groups of EC, PC and DEC and therefore organic solvents EC, PC and DEC preferentially react with Li, giving Li salts.

In LiPF$_6$-containing electrolyte solutions, DSC measurements gave somewhat different results as shown in Fig. 3. Mixtures of

electrolyte solution and delithiated graphite yielded weak exothermic peaks at 85–103 °C and strong ones at 244–264 °C (Fig. 3(a)). The peaks at 85–103 °C and 244–264 °C may be due to the reaction of PF$_5$ generated by the dissociation of LiPF$_6$, and thermal decomposition of SEI and electrolyte solutions, respectively [49–54]. A large difference from Fig. 2(b) was observed in Fig. 3(b) obtained from only lithiated graphite samples (Li$_{0.90-0.98}$C$_6$). Strong exothermic peaks were not observed at 150–160 °C, but DSC curves only slightly shifted to the exothermic side in the range of 120–260 °C, which suggests that the reaction of deintercalated Li with SEI is suppressed by LiF contained in SEI. XPS spectra obtained on used electrodes showed the presence of LiF which would have been formed by the dissociation of LiPF$_6$ and reaction of resulting PF$_5$ with Li. The exothermic peaks at 275–297 °C would be attributed to thermal decomposition of SEI [49–54]. Mixtures of electrolyte solution and lithiated graphite (Li$_{0.90-0.98}$C$_6$) gave weak exothermic peaks at 111–137 °C and strong ones at 250 °C or higher temperatures as shown in Fig. 3(c). The strong peaks observed between 250 and 300 °C consist of two exothermic peaks. Among the peaks observed at 111–137 °C, 1 molL^{-1} LiPF$_6$-EC/DMC/**C** containing fluoro-carbonate gave the weakest peak, showing the highest effect to prevent the reactions with Li deintercalated from graphite. It is inferred that fluoro-carbonate **C** has (−O)$_2$C=O group and a larger dielectric constant than fluoro-ethers A and B, therefore miscibility of fluoro-carbonate **C** with EC is better than that of fluoro-ethers on
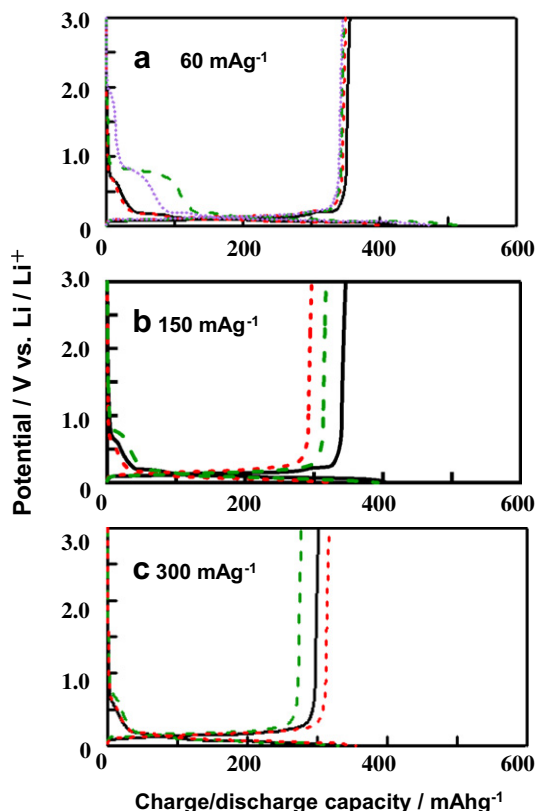
Fig. 9. First charge/discharge curves of NG15 µm in 1 molL^{-1} LiPF$_6$-EC/DMC (1:1 vol.) and 1 molL^{-1} LiPF$_6$-EC/DMC/(**A**, **B** or **C**) (1:1:1 vol.) at 60 mAg^{-1} (a), 150 mAg^{-1} (b) and 300 mAg^{-1} (c). ———: EC/DMC, --------: EC/DMC/**A**, – – – : EC/DMC/**B**, ·············: EC/DMC/**C**.

molecular level. Furthermore fluoro-ethers would mainly interact with hydrocarbon groups of EC and DMC as mentioned above. These may be the reasons why fluoro-carbonate **C** has the better effect on the reaction with deintercalated Li than fluoro-ethers **A** and **B**. The exothermic peaks between 250 and 300 °C are due to the decomposition of SEI and electrolyte solutions [49–54]. However, an endothermic peak due to exfoliation of graphite caused by final decomposition of Li-intercalated graphite is overlapped in the same temperature range [49]. Therefore the exothermic peaks are clearly separated into two peaks. Fig. 4 shows DSC data obtained using mixtures of 1 molL^{-1} LiPF$_6$-EC/EMC/PC or 1 molL^{-1} LiPF$_6$-EC/EMC/PC/(**A** or **B**) with delithiated graphite (Fig. 4(a)) or lithiated graphite (Li$_{0.88-0.92}$C$_6$) (Fig. 4(b)). The exothermic peak showing the decomposition of SEI and 1 molL^{-1} LiPF$_6$-EC/EMC/PC in Fig. 4(a) is located at 262 °C which is higher temperature than that for 1 molL^{-1} LiPF$_6$-EC/DMC in Fig. 3(a). However, DSC profiles are similar to each other for the electrolyte solutions with or without fluoro-ether below 275 °C as shown in Fig. 4(b).

3.2. Electrochemical oxidation stability of fluorine compound-mixed electrolyte solutions

Fig. 5 shows electrochemical oxidation currents measured by using Pt wire electrode in LiClO$_4$-containing electrolyte solutions. Small oxidation currents started to flow from 5.8 V vs Li/Li$^+$, gradually increasing with electrode potential. In the electrolyte solutions without fluoro-ethers, oxidation currents rapidly increased at ca. 8 V, indicating vigorous decomposition of the solvents. However, oxidation currents were largely reduced by mixing of fluoro-ethers. Oxidation current decreased with
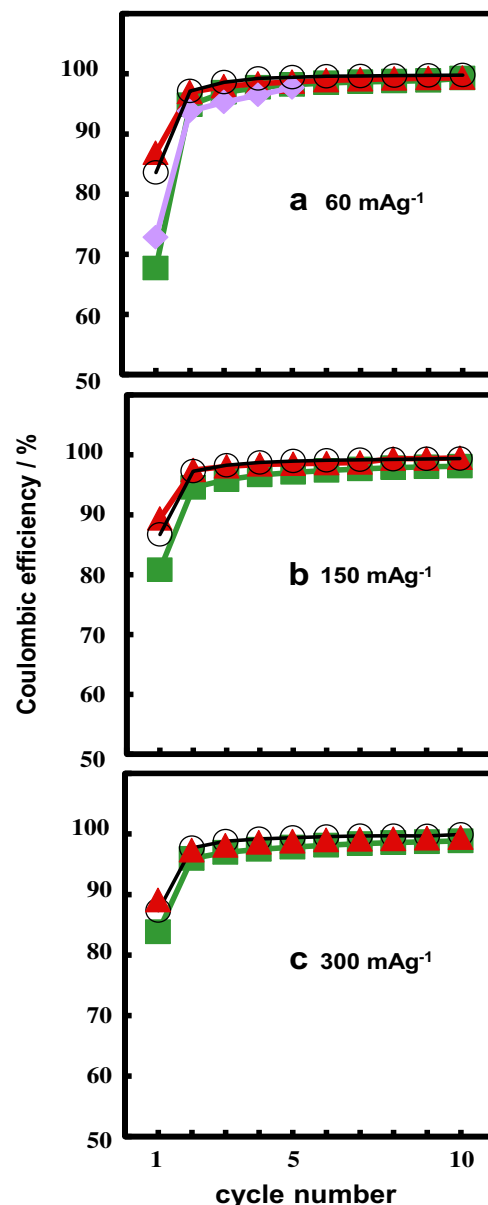

Fig. 10. Coulombic efficiencies of NG15 µm in 1 molL^{-1} LiPF$_6$-EC/DMC (1:1 vol.) and 1 molL^{-1} LiPF$_6$-EC/DMC/(**A**, **B** or **C**) (1:1:1 vol.) at 60 mAg^{-1} (a), 150 mAg^{-1} (b) and 300 mAg^{-1} (c). ———○———: EC/DMC, ———▲———: EC/DMC/**A**, ———■———: EC/DMC/**B**, ———◆———: EC/DMC/**C**.

increasing fluoro-ether for both **A** and **B**. This would be caused by decrease in the electrode area by adsorption of stable fluoro-ethers on Pt.

In LiPF$_6$-containing electrolyte solutions, oxidation currents were measured using glassy carbon electrode because Pt wire was lost by the reaction with fluorine above ca. 7.5 V. The results are shown in Fig. 6, in which large overpotentials were observed, i.e., the oxidation currents started to flow at 6.5 V higher than 5.8 V observed in LiClO$_4$-containing electrolyte solutions (Fig. 6(b)). Moreover, oxidation currents suddenly fell to zero above 8 V (Fig. 6(a)). This is so-called anode effect which is observed in electrolytic production of fluorine gas using carbon anode. PF$_6^-$ anion is oxidized at a high potential, yielding active fluorine and/or radical to react with glassy carbon electrode. Thin C–F film with a low surface energy is formed at the glassy carbon surface, preventing the contact of glassy carbon with electrolyte solution,
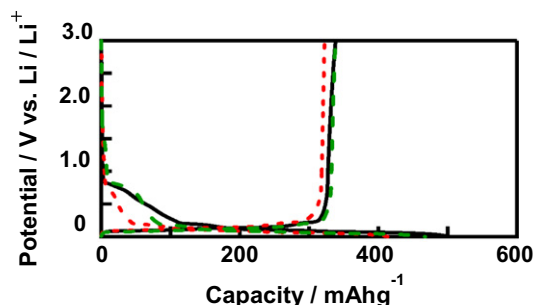
Fig. 11. First charge/discharge curves of NG15 μm in 1 molL^{-1} LiPF$_6$-EC/EMC/PC (1:1:1 vol.) and 1 molL^{-1} LiPF$_6$-EC/EMC/PC/(**A** or **B**) (1:1:1:1.5 vol.) at 60 mAg^{-1}. ————: EC/EMC/PC, ----------: EC/EMC/PC/**A**, – – – – – : EC/EMC/PC/**B**.

which leads to the sudden drop in oxidation currents. Nevertheless, the result shows that oxidation currents were smaller in fluoro-ether-mixed solutions than in 1 molL^{-1} LiPF$_6$-EC/DMC. The results obtained in LiClO$_4$- and LiPF$_6$-containing electrolyte solutions suggest that oxidative decomposition of fluorine compound-mixed solutions on oxide cathodes is less than decomposition of ordinary electrolyte solutions without fluorine compound.

3.3. Charge/discharge behavior for natural graphite electrode in fluorine compound-mixed electrolyte solutions

Fig. 7 shows charge/discharge potential curves at 1st cycle in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC with or without fluoro-ether. In all cases, potential plateaus at 0.8 V vs Li/Li$^+$ indicating the electrochemical reduction of PC were reduced by mixing of fluoro-ethers. This trend became more distinct with increasing fluoro-ethers in the electrolyte solutions from 10.0 vol.% to 33.3 vol.%. Coulombic efficiencies are shown in Fig. 8 as a function of cycle number. First coulombic efficiencies of NG15 μm were 65, 56 and 49% (60 mAg^{-1} in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC, respectively), 50, 40 and 46% (150 mAg^{-1} in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC, respectively), and 53, 49 and 23% (300 mAg^{-1} in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC, respectively). Mixing of fluoro-ethers largely improved first coulombic efficiencies, which indicates that fluoro-ethers effectively facilitate SEI formation on natural graphite powder because electrochemical reduction of fluoro-ethers **A** and **B** starts at 2.1 and 2.3 V vs Li/Li$^+$, respectively [40] higher than 1.3—1.6 V for PC, EC and DEC [55,56]. First coulombic efficiencies of NG15 μm in fluoro-ether-mixed electrolyte solutions were as follows: 74, 80 and 83% (60 mAg^{-1} in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/**A** (**A**: 10.0, 21.7 and 33.3 vol.%), respectively), 68, 72 and 80% (150 mAg^{-1} in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/**A** (**A**: 10.0, 21.7 and 33.3 vol.%), respectively), and 60, 70 and 74% (300 mAg^{-1} in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/**A** (**A**: 10.0, 21.7 and 33.3 vol.%), respectively); 78, 78 and 79% (60 mAg^{-1} in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/**B** (**B**: 10.0, 21.7 and 33.3 vol.%), respectively), 74, 80 and 84% (150 mAg^{-1} in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/**B** (**B**: 10.0, 21.7 and 33.3 vol.%), respectively), and 68, 74 and 79% (300 mAg^{-1} in 0.90, 0.78 and 0.67 molL^{-1} LiClO$_4$-EC/DEC/PC/**B** (**B**: 10.0, 21.7 and 33.3 vol.%), respectively). The increments in first coulombic efficiencies by mixing of fluoro-ethers were approximately 10—30%, 20—40% and 10—50% at 60, 150 and 300 mAg^{-1}, respectively. The charge capacities obtained in fluoro-ether-mixed solutions were nearly the same as those in original electrolyte solutions without fluorine compounds at 60 mAg^{-1}, however, slightly decreasing at higher current densities.

In LiPF$_6$-containing electrolyte solutions, first coulombic efficiencies were high in most of the cases. Fig. 9 shows charge/discharge potential curves at 1st cycle obtained in 1 molL^{-1} LiPF$_6$-

EC/DMC and 1 molL^{-1} LiPF$_6$-EC/DMC/(**A**, **B** or **C**) at 60, 150 and 300 mAg^{-1}. At 60 mAg^{-1}, fluoro-ether **B**- and fluoro-carbonate **C**-mixed electrolyte solutions were reduced at higher potentials than original and fluoro-ether **A**-mixed solutions. However, the potentials at 1st cycle quickly decreased in the same manner in all electrolyte solutions with and without fluoro-ethers at 150 and 300 mAg^{-1}. As shown in Fig. 10(a)—(c), first coulombic efficiencies in fluoro-ether **A**-mixed solution were high values, 87, 89 and 89% at 60, 150 and 300 mAg^{-1}, respectively. On the other hand, first coulombic efficiencies in fluoro-ether **B**- and fluoro-carbonate **C**-mixed electrolyte solutions were 68 and 73% at 60 mAg^{-1}, respectively. Nevertheless, those for fluoro-ether **B**-mixed solution increased to 81 and 84% at 150 and 300 mAg^{-1}, respectively (Fig. 10(b) and (c)), which indicates that SEI is quickly formed at high current densities. The charge capacities obtained in the electrolyte solutions with and without fluorine compounds indicate that fluoro-ethers **A** and **B** can be used for 1 molL^{-1} LiPF$_6$-EC/DMC. Fig. 11 shows charge/discharge curves at 1st cycle obtained in 1 molL^{-1} LiPF$_6$-EC/EMC/PC and 1 molL^{-1} LiPF$_6$-EC/EMC/PC/(**A** or **B**). In the PC-containing electrolyte solutions, SEI formation was faster in fluoro-ether-mixed solutions than in original one. First coulombic efficiencies obtained in fluoro-ether **A**- and **B**-mixed solutions were 78 and 74%, respectively, larger than 68% in original solution. Reduction of PC starts at 1.6 V vs Li/Li$^+$ slightly higher than 1.3—1.4 V for EC, DMC and DEC [55,56]. The results indicate that fluoro-ethers facilitate to SEI formation in PC-containing electrolyte solutions.

4. Conclusions

Thermal stability and electrochemical oxidation stability of fluorine compound-mixed electrolyte solutions and charge/discharge characteristics of natural graphite electrode (NG15 μm) have been investigated using 1 molL^{-1} LiClO$_4$-EC/DEC/PC, 1 molL^{-1} LiPF$_6$-EC/DMC and 1 molL^{-1} LiPF$_6$-EC/EMC/PC. DSC revealed that no exothermic reaction occurred between metallic Li and fluoro-ethers while EC/DMC mixture and fluoro-carbonate started to react with Li at 180 °C and a higher temperature, 226 °C, respectively. Reactions of lithiated graphite with surface film and electrolyte solutions were observed at 153—162 °C in LiClO$_4$-containing solutions. Intensity of exothermic peaks was large in both electrolyte solutions with and without fluoro-ethers. This may be because fluoro-ethers mainly interact with hydrocarbon groups of EC, PC and DEC and therefore EC, PC and DEC having >C=O group preferentially react with deintercalated Li, yielding Li salts. However, weak exothermic peaks caused by the reaction of lithiated graphite with surface film and electrolyte solutions were observed at 111—137 °C in LiPF$_6$-containing solutions. This is probably because LiF contained in the surface film prevents the reaction with Li deintercalated from graphite. Among the fluorine compound-containing solutions, fluoro-carbonate-mixed solution showed the lower reactivity with deintercalated Li than fluoro-ether-mixed ones. Electrochemical oxidation currents were decreased by the mixing of fluoro-ethers in both LiClO$_4$- and LiPF$_6$-containing solutions. Large overpotentials accompanying anode effect were observed for glassy carbon electrode in 1 molL^{-1} LiPF$_6$-EC/DMC and 1 molL^{-1} LiPF$_6$-EC/DMC/(**A** or **B**). Charge/discharge experiments indicated that first coulombic efficiencies of NG15 μm were mostly high in fluoro-ether-mixed electrolyte solutions, and fluoro-ethers facilitated SEI formation in PC-containing solutions.

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